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DATE: 29 September 2003

TO: Environmental Protection Agency
                 ATTN: Emission Factor and Inventory Group (Mr. Ron Ryan)

FROM: Mr. William Hodan, PES
                 PES Project POI563.005

CONTRACT: 68-D-02-104 / WA 1-05

SUBJECT: Recommendations for the Update and Improvement of Existing
                 PM2.5 Split Factors

EXECUTIVE SUMMARY

This report represents the second part of a two-part study conducted by PES to review the top ten PM2.5 split factor profiles used to speciate PM2.5 emission inventories for modeling purposes. The top 10 PM2.5 split factors represent approximately 80% of the entire PM2.5 inventory, so the implications of reviewing these 10 factors are far-reaching. The first part of the study consisted of a review of the split factors that are currently being used. PES obtained the background documents that were used to derive the existing split factors. Using those documents PES attempted to reconstruct the PM2.5 split factors and determine if they had been calculated correctly. PES found that some of the existing split factors had been calculated incorrectly and there was a general lack of background documentation. For further information on the first part of this study refer to the report titled: "Expansion of Existing PM2.5 Split Factor Background Documentation".

This report represents the second part of the two-part study. PES has gathered reports and technical papers containing the results from studies that have been conducted recently to determine the fractions of organic carbon (OC), also represented as primary organic carbon (POA) by multiplying the OC by 1.2; elemental carbon (EC); sulfates (SO_4) and nitrates (NO_3). The information gathered in the literature search is presented in this report, and recommendations are made to revise several of the existing split factors according to the updated information. Table 1 contains the recommended split factors based on the information collected in this study. As discussed in this report, PES has not recommended changes to all ten split factors as a result of the study. In fact, the study of recent materials confirmed the validity of some of the existing profiles. PES was unable to locate recent PM2.5 split profile data for the non-road diesel, solid waste combustion, and sand and gravel categories. Upon review of the recent study materials gathered, PES recommends changes to the profiles for agricultural burning, coal combustion, paved roads, and wood waste boilers. In addition to the review of the top 10 PM2.5 split factor profiles, PES also recommends that a profile from the BRAVO study be used to replace the existing wildfires profile.

Table 1 highlights the 1996 PM2.5 emissions and the revised split factors that are recommended in this report. Table 2, which is in the body of this report contains the old split factors and total emissions. The new split factor profiles result in a large increase in the POA and SO_4 and a decrease in the EC and NO_3 that would be expected from these sources.

Table 1. 1996 PM2.5 Emissions and Corresponding Revised Split Factors

Profile Name	1996 Tons PM2.5 *Unadjusted* (tons)	1996 Tons PM2.5 *Adjusted* (tons)	Primary Organic Aerosol (POA) (% of PM2.5)	Elemental Carbon (EC) (% of PM2.5)	Sulfate (SO_4) (% of PM2.5)	Nitrate (NO_3) (% of PM2.5)
Soil Dust	4,333,253	896,614	5.45	0.37	0.04	0.11
Agricultural Burning	949,866	889,775	67	4	1	0.3
Paved Road Dust	597,727	149,066	12	1.12	0.70	0.04
Residential Wood Combustion	432,630	431,078	56.56	10.77	0.37	0.22
Non-road Diesel 49-State 1996	347,785	325,316	22.44	74.11	3.29	0.16
Solid Waste Combustion	232,708	232,562	0.68	3.50	6.80	0.00
Coal Combustion	182,069	181,526	20	1	16	0.5
Sand & Gravel	156,367	155,489	0.00	0.00	0.55	0.00
On-road HDDV 1996	149,295	164,479	22.71	75.00	0.41	0.17
Wood Waste Boiler	130,201	130,195	39	14	8	0
	Top 10 Categories **Total Tons PM2.5 (Unadjusted) 7,511,901**	*Top 10 Categories* **Total Tons PM2.5 (Adjusted) 3,556,100**	*Top 10 Categories* **Total Tons POA (Adjusted) 1,105,737**	*Top 10 Categories* **Total Tons EC (Adjusted) 479,638**	*Top 10 Categories* **Total Tons SO_4 (Adjusted) 79,401**	*Top 10 Categories* **Total Tons NO_3 (Adjusted) 6,371**
		National **Total Tons PM2.5 (Adjusted) 4,444,496**	*National* **Total Tons POA (Adjusted) 1,596,949**	*National* **Total Tons EC (Adjusted) 520,565**	*National* **Total Tons SO_4 (Adjusted) 177,501**	*National* **Total Tons NO_3 (Adjusted) 11,018**

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PURPOSE

The purpose of this report is to provide a detailed description of updated PM2.5 split factors intended to replace or otherwise improve existing PM2.5 split factors. The term, "PM2.5 split factors" refers to profiles that speciate PM2.5 emissions into organic carbon, elemental carbon, sulfate, and nitrate components. Information on split factors discussed in this memorandum were gathered during a literature search that was initially intended to locate PM and VOC speciated profiles for addition to the SPECIATE program. A second review of that literature was conducted to identify profiles containing specific information regarding PM2.5 split factors. Information relative to the specific parameters of the source tests conducted to develop the split factors is discussed in this memorandum, along with a description of the methods used to analyze the PM2.5 samples. The existing split factors and related information provided by the EPA are linked to the following website: http://www.epa.gov/ttnchie1/emch/speciation/index.html

This report represents the second half of a two-part analysis of PM2.5 split factors. A memorandum titled "Expansion of Existing PM2.5 Split Factor Background Documentation" was submitted to the EPA in fulfillment of the first part of the PM2.5 split factor analysis. In that memorandum, PES addressed existing split factors for the ten largest sources of PM2.5 emissions. Research was conducted to locate the original documentation used to develop those PM2.5 split factors. Several errors were located and addressed in the memorandum. The results from the second part of the analysis discussed in this memorandum is intended to provide additional data that can be used to replace or improve the split factors for large PM2.5 emission sources.

The ten PM2.5 split factor source types of interest listed in order of decreasing emission magnitude are provided in Table 2 with the split factors that are currently being used. Table 2 addresses the elemental carbon (EC), organic carbon (OC) - represented as primary organic aerosol (POA), sulfate (SO_4), and nitrate (NO_3) percentages of the PM2.5 emissions assigned to these split factors in 1996. All other species present in the PM2.5 size fraction fall into the "Other" category. The unadjusted estimates represent the amount of PM2.5 that was reported in the original 1996 emission inventory. Some of the emission estimates were subsequently adjusted by the EPA to account for the settling of dust that occurs with certain fugitive dust categories (75% reduction). The PM2.5 emission estimates from other sources were adjusted by a few percent or less, but no significant changes were made. It should also be noted that the specie Primary Organic Aerosol (POA) in the split factor assignments on the website referred to above was derived by multiplying the organic carbon (OC) percent by 1.2 as an approximation used to account for the other elements bonded to C in the primary organic aerosol. It is important to recognize the relationship between POA and OC in split factor profiles to ensure that both species are not included in the split factor profile, which would result in double counting of those emissions in modeling applications.

There are over 10,000 Source Classification Codes, (SCC) used to classify emissions, however there are currently only 73 split factors available to be assigned to the SCCs. Although not all SCCs have a PM2.5 component, there are many PM2.5 sources that must be assigned to a split factor that closely resembles the source. Because of this, many large sources of PM2.5 are

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not specifically identified as one of the top 10 profile types listed in Table 2. For instance, unpaved roads are a large source of PM2.5, but there is no profile designed specifically to speciate emissions from unpaved roads. As a result, the emissions from unpaved roads are represented by the soil dust profile, 22059 in the 1996 inventory. This is just one example of how the PM2.5 sources in the inventory are speciated, but explains why some large source types are not included in the top 10 profiles and why the relative magnitudes of the sources in Table 2 may be somewhat different than expected.

Table 2. 1996 PM2.5 Emissions and Corresponding Split Factors

Split Factor Profile Number	Profile Name	1996 Tons PM2.5 *Unadjusted* (tons)	1996 Tons PM2.5 *Adjusted* (tons)	Primary Organic Aerosol (POA) (% of PM2.5)	Elemental Carbon (EC) (% of PM2.5)	Sulfate (SO₄) (% of PM2.5)	Nitrate (NO₃) (% of PM2.5)
22059	Soil Dust	4,333,253	896,614	5.45	0.37	0.04	0.11
22060	Agricultural Burning	949,866	889,775	63.89	7.50	1.54	0.63
22058	Paved Road Dust	597,727	149,066	17.68	1.12	0.70	0.22
22061	Residential Wood Combustion	432,630	431,078	56.56	10.77	0.37	0.22
35602	Non-road Diesel 49-State 1996	347,785	325,316	22.44	74.11	3.29	0.16
22009	Solid Waste Combustion	232,708	232,562	0.68	3.50	6.80	0.00
22001	Coal Combustion	182,069	181,526	1.07	1.83	11.90	0.00
22038	Sand & Gravel	156,367	155,489	0.00	0.00	0.55	0.00
35600	On-road HDDV 1996	149,295	164,479	22.71	75.00	0.41	0.17
22008	Wood Waste Boiler	130,201	130,195	11.77	20.19	2.82	0.09
		Top 10 Categories Total Tons PM2.5 (Unadjusted) **7,511,901**	*Top 10 Categories Total Tons PM2.5 (Adjusted)* **3,556,100**	*Top 10 Categories Total Tons POA (Adjusted)* **1,016,717**	*Top 10 Categories Total Tons EC (Adjusted)* **520,346**	*Top 10 Categories Total Tons SO₄ (Adjusted)* **70,019**	*Top 10 Categories Total Tons NO₃ (Adjusted)* **8,785**
			National Total (Adjusted) **4,444,496**	*National Total (Adjusted)* **1,481,890**	*National Total (Adjusted)* **569,085**	*National Total (Adjusted)* **168,119**	*National Total (Adjusted)* **13,432**

BACKGROUND

USEPA, States, multi-state organizations, academics, and others have in the past performed air quality modeling for particulate matter species using the Regional Modeling System for Aerosols and Deposition, (REMSAD), software. Updated versions of REMSAD and the Community Multiscale Air Quality model, (CMAQ), are expected to be used in the future. All of these models will require that the "PM" emissions values, as recorded in an emissions inventory, be split into component species as required by the air quality models. "Species" as used in this memorandum, refers to the separation into sulfates, nitrates, organic carbon, and elemental carbon, not to elemental speciation or to specific organic compounds. Emission inventory preprocessors, such as EPS2.5, SMOKE, and EMS-2001 apply a set of split factors based on each emission record's SCC code to the PM inventory in order to generate the needed species. The current set of split factors for performing this task was last reviewed in 1995, although a few updates were made for some mobile source categories as part of a rulemaking in 1999.

RESEARCH RESULTS

One of the problems with the existing recommended split factors (such as the split factors listed in Table 2), is that they were developed using several different source test methods. The use of different source test and analytical methods makes it difficult to compare results for the different sources. PM2.5 is particularly sensitive to test method consistency since some of the PM2.5 particle mass condenses from hot gaseous emissions after leaving the stack. This is particularly true for combustion sources which make up seven of the top ten PM2.5 emission sources. Sampling techniques for individual sources must consistently provide similar emission dilution ratios and residence times (or lack of emission dilution), to allow results from different tests to be compared. Additionally, chemical analysis of the filters used to collect the PM2.5 should be standardized so that these results can be compared as well. The sampling methods and corresponding chemical analyses used to develop the split factor profiles included in this memorandum are discussed when that information was presented in the literature. In most cases the sampling and analysis methods are consistent, but as there are no standardized procedures currently in place for split factor development, some variation is expected.

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Soil Dust

Research into recent literature for PM2.5 split factors for soil dust resulted in the location of nine profiles from two different literature sources. Both literature sources grouped road dust and soil dust profiles under the geological material category, so both categories have been included in Table 3 for comparison.

Table 3. Soil Dust PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
Off-road Soil Samples from Purtis Creek and Big Thicket, TX Profile ID: BVSOIL1 *(TOR Method)*	19.7601 ± 18.9875	0.2038 ± 2.5200	0.6322 ± 0.4232	0.1094 ± 0.4164	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Soil Samples from Langtree-Skiles Ranch, San Vincente, Big Bend K-Bar, and Laredo, TX Profile ID: BVSOIL2 *(TOR Method)*	7.9063 ± 2.8450	0.0115 ± 0.8716	0.1329 ± 0.0694	0.0000 ± 0.0686	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Composite of Paved Road Dust from Craig and Steamboat Springs, CO Profile ID: MZPVRDC *(TOR Method)*	7.39 ± 2.61	0.77971 ± 0.43154	0.06432 ± 0.04716	0.01576 ± 0.04717	Watson, J.G., J.C. Chow, J.E. Houck. PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere, vol. 43: pp. 1141-1151. 2001.
Composite of Two Unpaved Road Dust Samples from Buffalo Pass (BP) and Hayden VOR Access Roads (HV) Profile ID: MZUPRDC *(TOR Method)*	4.63 ± 2.17	0.43520 ± 0.14103	0.09576 ± 0.04914	0.06151 ±0.08699	Watson, J.G., J.C. Chow, J.E. Houck. PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere, vol. 43: pp. 1141-1151. 2001.
Composite of Four Soil Samples in the Vicinity of Buffalo Pass (BP), Juniper Mountain (JU), Baggs (BB), and Hayden Waste Water (HS) Receptor Sites Profile ID: MZSOILC *(TOR Method)*	6.06 ± 2.58	0.94372 ± 1.48	0.13031 ± 0.11503	0.04228 ± 0.04972	Watson, J.G., J.C. Chow, J.E. Houck. PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere, vol. 43: pp. 1141-1151. 2001.

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Table 3. Soil Dust PM2.5 Split Factors (continued)

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
Composite of all 12 Geological Samples (Six Paved Road Dust, Two Unpaved Road Dust, and Four Soil Samples) Profile ID: MZGEOLC *(TOR Method)*	6.49 ± 2.55	0.77696 ± 0.84365	0.09156 ± 0.06886	0.03222 ± 0.04878	Watson, J.G., J.C. Chow, J.E. Houck. PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere, vol. 43: pp. 1141-1151. 2001.
Paved Road Dust – San Antonio and Laredo, TX Profile ID: BVPVRD1 *(TOR Method)*	15.8664 ± 3.1864	2.3505 ± 1.7110	0.9993 ± 0.2203	0.1104 ± 0.2066	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Paved Road Dust Craig, CO Profile ID: MZCPVRDC *(TOR Method)*	7.73 ± 2.21	1.12 ± 0.30935	0.07922 ± 0.05478	0.00000 ± 0.05451	Watson, J.G., J.C. Chow, J.E. Houck. PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere, vol. 43: pp. 1141-1151. 2001.
Paved Road Dust Steamboat Springs, CO Profile ID: MZSPVRDC *(TOR Method)*	7.05 ± 3.44	0.43691 ± 0.31744	0.04942 ± 0.03804	0.03151 ± 0.05458	Watson, J.G., J.C. Chow, J.E. Houck. PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere, vol. 43: pp. 1141-1151. 2001.

The PM2.5 test samples from Watson, Chow, and Houck, 2001 were collected in the vicinity of the Yampa Valley in northwestern Colorado in 1995. The test samples were obtained in one-half to one kg amounts from the locations described in Table 3. The dust was stored in polyethylene bags, and prepared for testing by drying and then passing the dust through a sieve. The samples were tested by resuspending them in a laboratory chamber and sampling through PM2.5 inlets onto Teflon-membrane and quartz fiber filters. The filters were analyzed for mass by gravimetry. Next, half of each quartz fiber filter was extracted in deionized distilled water and analyzed for NO$_3$ and SO$_4$ using ion chromatography. The other half of the filter was used to quantify OC and EC using the IMPROVE thermal optical reflectance method (TOR). Potassium carbonate backup filters were extracted in a sodium carbonate solution and analyzed for absorbed SO$_2$ as SO$_4$ by ion chromatography. Silver nitrate impregnated cellulose fiber filters were analyzed for H$_2$S as SO$_4$ by ion chromatography. All sampling procedures followed an established laboratory sample chain of custody and data validation process. Blank and replicate analyses were performed for approximately 10% of all samples according to standard operating procedures.

The PM2.5 test samples from the BRAVO study, (Chow et. al. 2002), were collected at various intersections in San Antonio and Laredo, TX in 1999. The samples were obtained by the grab/resuspension method, air dried in the laboratory under 20-30% relative humidity

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atmosphere, sieved through a Tyler 400 mesh screen ($< 38 \mu m$ geometric diameter), and resuspended in a laboratory chamber. The PM was collected on filters through PM2.5 and PM10 impactor inlets at a flow rate of 10 L/min. Chemical abundances for each sample were determined by dividing the concentration of each chemical by the total mass concentration, with error propagation calculated by addition in quadrature. OC and EC fractions were determined by the IMPROVE thermal optical reflectance method (TOR). The individual profiles were then composited to form the profiles addressed in the BRAVO study and this memorandum.

An analysis of the two soil dust specific profiles (Profile IDs MZSOILC and BVSOIL2), shows that although the samples for these two profiles were collected in different States (CO and TX), and hundreds of miles apart, there is a strong correlation between the values for OC, EC, SO_4 and NO_3 in the profiles. In fact, taking the uncertainty of the values for each of the split factors into consideration, the split factors are in complete agreement within the range of uncertainty. Additionally, the split factors are not significantly different than the soil dust split factors represented by EPA PM2.5 split factor profile number 22059 as shown in Table 2 of this report. The soil samples for EPA split factor profile number 22059 were collected in Iowa and Oregon which of course are quite distant from each other as well as from Colorado and Texas. [The significant difference between the BVSOIL1 profile and the other soil profiles cannot be evaluated due to the large uncertainty associated with BVSOIL1]. The strong correlation between values collected from different areas of the country suggests that there is not a great deal of variation in soil dust profiles across the United States, at least with respect to the four species of interest in the PM2.5 split factors. OC and EC from paved road dust samples are slightly higher than the OC and EC in soil samples due to the contribution of motor vehicle related deposits. Nevertheless, there is a strong correlation between paved, unpaved, and off-road split factor profiles which makes it difficult to differentiate statistically between split factor profiles from these sources using only the four split factor species. This also justifies application of the soil dust profile to split PM2.5 emissions estimates from unpaved roads.

Recommendations for Revisions to the Soil Dust Profile

The soil dust information presented in this report agrees with split factor profile 22059, which is currently applied to soil dust emissions. There is some variation between the profiles presented in this report and the split factor values in profile 22059 (See Table 2 of this report), but the uncertainty of the estimates presented in this report show that the results from those studies were not statistically different than profile 22059. Although the results presented in this report are not significantly different than profile 22059, it does appear that 22059 may be underestimating the percentage of OC in soil dust PM2.5 by 1-2%.

Agricultural Burning

The current agricultural burning split factor, EPA PM2.5 split factor profile number 22060, would probably be more appropriately designated as a miscellaneous profile for outdoor burning of biomass. This is due to the fact that the individual profiles composited to form 22060 are from a wide variety of sources including slash burning, agricultural field burning, and prescribed burning. There is significant variability in profiles from these sources as evidenced by the background information on the current split factor profile, so it seems apparent that there is a need for a separate split factor profile for agricultural burning as well as emissions from other forms of outdoor burning that have traditionally been assigned to profile 22060.

PES researched recent literature to locate split factor emission profiles specifically for agricultural burning. Unfortunately, most of the related profiles located were vegetative/biomass burning profiles, and did not contain information specific to agricultural burning. However, profiles from other types of burning could be used to more accurately split those PM2.5 emissions for specific source types. Two of the literature articles located contained profiles from the slash burning of trees.

> Reference 1. Oros, D. R., B.R.T. Simoneit. Identification and Emission Factors of Molecular Tracers in Organic Aerosols from Biomass Burning Part 1. Temperate Climate Conifers. Applied Geochemistry, vol. 16: pp. 1513-1544, 2001.

> Reference 2. Oros, D. R., B.R.T. Simoneit. Identification and Emission Factors of Molecular Tracers in Organic Aerosols from Biomass Burning Part 2. Temperate Climate Conifers. Applied Geochemistry, vol. 16: pp. 1545-1565, 2001.

These two articles contained detailed information on the chemical species present in smoke from the burning of trees, but the information was not necessarily specific to PM2.5 emissions. Although the articles both state that most of the emissions from burning biomass are fine particles, it is not clear from the articles that the emissions represented in the profiles are strictly PM2.5 emissions. Additionally, NO_3 and SO_4 are not represented in these profiles.

A recent article in Environmental Science and Technology reviewed the results of a study that was conducted to determine the emission rate of PM2.5 from the burning of several different types of wood in a controlled laboratory environment. The study was intended to quantify the emission rate of PM2.5 from the open burning of the different types of wood in a wildfire or prescribed burn scenario. Again, open burning of trees/wood is obviously different than agricultural burning. Therefore, a separate split factor profile for open burning of forests would provide a more accurate split of PM2.5 emissions from that source.

> Reference: Hays, M.D., C.D. Geron, K.J. Linna, N.D. Smith, J.J. Schauer. Speciation of Gas-Phase and Fine Particle Emissions from Burning of Foliar Fuels. Environmental Science and Technology, vol. 36: pp. 2281-2295, 2002.

In the Hays et. al., 2002 study, samples of six different mixtures of foliar fuels were collected for burning. A custom fabricated dilution sampler was used to collect the emissions

from each burn. PM2.5 mass emissions were determined gravimetrically using Teflon filters conditioned in a control chamber for 24 hours at ambient temperatures and 30-40% relative humidity. The inorganic portion of PM2.5 in the samples was classified by ion chromatography (IC) and wavelength dispersive x-ray fluorescence (XRF). The organic portion of the samples was analyzed using solvent extraction and gas chromatography/mass spectrometry (GC/MS) methodologies. OC and EC values were measured using the National Institute for Occupational Safety and Health (NIOSH) method 5040, which uses thermal-optical transmittance (Sunset Labs).

The results from Hays et. al., 2002 do not contain the mass fractions of OC and EC in the PM2.5 explicitly. Instead, the mass emission rate and associated uncertainty of total PM2.5, OC, and EC are expressed as grams of each emitted per kg of biomass combusted. Due to the wide range of uncertainty associated with the emission rates, it will be necessary to obtain further information to quantify the OC and EC fractions in the PM2.5. A rough estimation of the OC and EC fractions (disregarding uncertainty) from all the tests combined shows that OC and EC comprise 75% and 2% of the total PM2.5 respectively. SO_4 was non-detect (ND) in the emissions from five of the six samples, and below quantifiable limits in the remaining sample. The average NO_3 composition was roughly 1.6% without taking the associated uncertainty into consideration. These split factor values are considerably different than the split factors for agricultural burning in split factor profile number 22060.

PES located one literature source containing vegetative burning profiles from sampling in the plumes of small controlled burns of wood debris at Big Bend National Park. The information from this literature article has been included in Table 4 for comparison to EPA PM2.5 split factor profile number 22060.

Only one literature source contained a profile described as agricultural burning. A composite profile for the burning of asparagus fields is included in Table 4 for comparison to EPA PM2.5 split factor profile number 22060.

Table 4. Agricultural Burning PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO₄ Percent	NO₃ Percent	Reference Information
Vegetative Burning – Pine Fence Profile ID: BURN1 *(TOR Method)*	43.4527 ± 5.5761	55.1843 ± 6.3893	0.2902 ± 0.1030	0.0066 ± 0.0429	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Vegetative Burning – Pine Fence Profile ID: BURN2 *(TOR Method)*	87.7173 ± 16.9684	11.5745 ± 8.2651	0.2935 ± 0.0592	0.0451 ± 0.0174	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.

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Table 4. Agricultural Burning PM2.5 Split Factors (continued)

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
Vegetative Burning - Mesquite Profile ID: BURN3 *(TOR Method)*	45.9419 ± 4.0042	15.2580 ± 7.7814	2.0975 ± 0.4422	0.4757 ± 0.1457	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Vegetative Burning – Mesquite Profile ID: BURN4 *(TOR Method)*	65.4985 ± 11.3237	9.0696 ± 2.9703	1.4770 ± 0.3374	0.4194 ± 0.0833	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Vegetative Burning – Tamarisk Profile ID: BURN5 *(TOR Method)*	60.1802 ± 7.8838	4.7457 ± 1.4865	6.4306 ± 1.7063	0.1817 ± 0.0406	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Vegetative Burning – Huisache Profile ID: BURN6 *(TOR Method)*	78.5411 ± 10.9289	10.9306 ± 6.2537	1.4394 ± 0.5482	0.4429 ± 0.0896	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Vegetative Burning – Grass Profile ID: BURN7 *(TOR Method)*	68.2084 ± 14.2931	7.6043 ± 3.6228	3.2539 ± 2.0391	0.1530 ± 0.0977	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Vegetative Burning – Composite of all Vegetative Burning Profiles Profile ID: BURN *(TOR Method)*	64.4064 ± 16.4483	15.7505 ± 15.4458	2.3889 ± 2.2702	0.2365 ± 0.1817	Chow, J.C. et. al. Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Agricultural Field Burning – Asparagus Field; Imperial CA *(TOR Method)*	55.566 ± 15.013	4.422 ± 1.562	1.122 ± 0.384	0.322 ± 0.220	Watson, J.G, J.C. Chow. Source Characterization of Major Emission Sources in the Imperial and Mexicali Valleys Along the US/Mexico Border. The Science of the Total Environment; vol. 276, pp. 33-47, 2001.

The vegetative burning profiles represented in the BRAVO study (Chow et. al., 2002) were assembled from testing of small controlled burns of wood and other debris at Big Bend National Park in 1999. The wood debris included three common tree species from the area: mesquite, tamarisk, and huisache. Other fuels burned consisted of native dry grass and pine fence posts that had been treated with creosote. Ground-based source-dominated sampling was used to gather the test samples. Because of the effect of gaseous organic carbon adsorption on quartz-fiber filters, the profiles were normalized to the sum of the species rather than the

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measured mass. OC and EC fractions were determined by the IMPROVE thermal optical reflectance method (TOR).

A comparison among the BRAVO study profiles shows a high degree of variability, even between profiles based on burning of the same fuel. In general, compared to profile 22060 these wood burning profiles are higher in EC, OC, and SO_4, and lower in NO_3. One reason that true agricultural burning profiles may tend to be higher in NO_3 content could be the agricultural use of nitrogen based fertilizers. Enrichment of soil and plants with nitrogen based fertilizers would likely increase emissions of various nitrogen containing compounds when a field is burned.

The profile from asparagus field burning from Watson and Chow, 2001, was developed from a series of 17 tests from the burning of asparagus fields. Ground-based source sampling was used to gather the emissions from this source. Five of the 17 samples collected were used in the profile included in the literature and Table 4 of this memorandum. Ion chromatography (IC) was used to determine the SO_4 and NO_3, and thermal/optical reflectance (TOR) was used to determine the EC and OC in the emissions.

A comparison of the Watson and Chow, 2001 profile to split factor profile 22060 shows that the profiles are mostly in agreement, with the exception of the EC split factor. Profile 22060 reports an EC split factor value of approximately twice the value of the Watson and Chow, 2001 profile. Profile 22060 also reports an NO_3 split factor of approximately twice that of Watson and Chow, 2001, however the NO_3 split factor is less than 1% in both cases.

Recommendations for Revisions to the Agricultural Burning Profile

The existing agricultural burning profile, number 22060, represents an average of profiles from slash burning, agricultural field burning, and prescribed burning. A comparison of profile 22060 (See Table 2 of this report), to the agricultural field burning profile from Watson and Chow, 2001 shows minor differences. Additionally, there is a significant difference in the vegetative burning profile from the BRAVO study and Watson and Chow, 2001. The vegetative burning profile from the BRAVO study was formed by taking measurements from a series of small burns of woods, grass, and other materials.

Using the information from Watson and Chow, 2001 and the BRAVO study, separate profiles can be generated to characterize the PM2.5 emissions from agricultural burning and slash/prescribed burning. PES recommends using the agricultural field burning profile from Watson and Chow, 2001 to replace profile 22060 since this profile strictly represents an agricultural burning scenario. Additionally, the composite vegetative burning profile from the BRAVO study can be used to replace the current profile for wildfires - 22070. Profile 22070 only considers emissions of EC and OC, neglecting emissions of SO_4, and NO_3.

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Residential Wood Combustion

The current residential wood combustion profile, EPA PM2.5 split factor profile number 22061, is based primarily on a study of residential woodstove use that was published in 1989 (Core, et. al., 1989). The EC and OC split factors are based solely on residential woodstove use, and the NO_3 and SO_4 split factors are based on the 1989 study combined with a residential fireplace study that compared the combustion of softwood and hardwood (Hildemann, et. al., 1991). Since PM2.5 emissions from residential wood combustion are a large source of PM2.5 emissions, it may improve modeling efforts to provide separate split factor profiles for woodstove and fireplace use. Providing split factors for different types of wood could also be useful in some applications, but because the split factors are primarily used to split whole inventories, it is unlikely that split factors for specific wood types could be used.

PES researched recent literature to locate split factor emission profiles for residential woodstove and fireplace use. Six recent literature articles covering residential fireplace and woodstove use were located. Due to the number of profiles in these six literature articles, a separate table is provided for each reference.

Table 5.1. Residential Wood Combustion PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO₄ Percent	NO₃ Percent	Reference Information
Fireplace: Hardwood – Red Maple *(IC and XRF analysis)*	85.5 ± 5.8	6.7 ± 1.9	0.31 ± 0.03	0.60 ± 0.04	Fine, P.M., G.R. Cass, B.R.T Simoneit; Chemical Characterization of Fine Particle Emissions from Fireplace Combustion of Woods Grown in the Northeastern United States. Environmental Science and Technology, vol. 35, pp. 2265-2675, 2001.
Fireplace: Hardwood – Northern Red Oak *(IC and XRF analysis)*	87.5 ± 5.4	3.8 ± 0.7	0.42 ± 0.06	0.40 ± 0.07	Same
Fireplace: Hardwood – Paper Birch *(IC and XRF analysis)*	86.8 ± 6.0	22.0 ± 2.9	1.68 ± 0.05	0.28 ± 0.05	Same
Fireplace: Softwood – Eastern Red Pine *(IC and XRF analysis)*	73.4 ± 6.4	31.3 ± 2.8	0.13 ± 0.01	0.17 ± 0.01	Same
Fireplace: Softwood – Eastern Hemlock *(IC and XRF analysis)*	102.3 ± 6.4	5.4 ± 0.9	0.33 ± 0.08	0.38 ± 0.10	Same
Fireplace: Softwood – Balsam Fir *(IC and XRF analysis)*	106.3 ± 6.5	7.0 ± 0.8	0.30 ± 0.08	0.40 ± 0.10	Same

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In the tests represented in Table 5.1, each wood species was burned in a conventional masonry fireplace in a residential building. Smoke samples were collected from a point in the chimney approximately four meters above the fire using a dilution source sampler. The hot emissions were mixed with 20-30 fold excess of filtered air. This caused the organic vapors to condense onto particles from the source exhaust. In this way, the emissions could be sampled at near atmospheric conditions yielding an accurate representation of the organic gas and particle phases. The samples were withdrawn from the dilution source sampler and divided into three streams. Quartz filters were used to capture the portion of the sample intended for EC and OC analysis. A Teflon filter was used to capture the portion of the sample for use in mass determination and ion chromatography (IC) or x-ray fluorescence (XRF) analysis. The third stream was a duplicate Teflon filter to be analyzed as needed. The weight percents of OC from two tests in this study exceeded 100% of the total PM2.5 because of the adsorption of gas-phase organics onto the quartz filter.

The results from this study in comparison with EPA split factor profile 22061 show a significant difference, particularly with respect to the OC split factor. The OC split factor from fireplace combustion of wood from this study averages roughly 90% of the PM2.5. As explained earlier, this is due to the adsorption of organic compounds onto the quartz filter. It is impossible to determine from the literature what this value actually represents with respect to OC alone. The EC percentage averages from this study were slightly higher than split factor profile 22061, but the difference in the test results between different types of wood combustion varied widely, between 3.8% and 31.8%. The presence of SO_4 and NO_3 in the results from this study both averaged less than 1% of the PM2.5, which is in line with the SO_4 and NO_3 split factors in profile 22061.

Table 5.2. Residential Wood Combustion PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO₄ Percent	NO₃ Percent	Reference Information
Fireplace: Hardwood – Yellow Poplar *(IC and XRF analysis)*	84.9 ± 5.1	3.4 ± 0.4	0.36 ± 0.02	0.32 ± 0.02	Fine, P.M., G.R. Cass, B.R.T Simoneit. Chemical Characterization of Fine Particle Emissions from Fireplace Combustion of Woods Grown in the Southern United States. Environmental Science and Technology, vol. 36, pp. 1442-1451, 2002.
Fireplace: Hardwood – White Ash *(IC and XRF analysis)*	76.8 ± 5.4	6.4 ± 0.9	0.77 ± 0.05	0.65 ± 0.04	Same
Fireplace: Hardwood – Sweetgum *(IC and XRF analysis)*	78.8 ± 6.0	2.7 ± 0.6	0.50 ± 0.04	0.63 ± 0.04	Same
Fireplace: Softwood – Mockernut Hickory *(IC and XRF analysis)*	74.2 ± 6.4	1.2 ± 0.2	0.18 ± 0.01	0.26 ± 0.01	Same

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Table 5.2. Residential Wood Combustion PM2.5 Split Factors (continued)

Fireplace: Softwood – Loblolly Pine *(IC and XRF analysis)*	100.4 ± 6.4	17.9 ± 1.6	0.19 ± 0.04	0.26 ± 0.04	Same
Fireplace: Softwood – Slash Pine *(IC and XRF analysis)*	100.6 ± 6.5	14.2 ± 1.7	1.11 ± 0.08	0.40 ± 0.07	Same

In the split factor profiles referred to in Table 5.2, the testing procedure was identical to the procedure used in the profiles included in Table 5.1. This paper is the second in an on-going series of tests being conducted to quantify the mass rate and composition of PM2.5 emissions from wood burning in different parts of the United States. Also, as in the previous study, the weight percents of OC from two tests in this study exceeded 100% of the total PM2.5 because of the adsorption of gas-phase organics onto the quartz filter.

The results from this study in comparison with EPA split factor profile 22061 show a significant difference, particularly with respect to the OC split factor. The OC split factor from fireplace combustion of wood from this study averages roughly 86% of the PM2.5. As explained earlier, this is due to the adsorption of organic compounds onto the quartz filter. It is impossible to determine from the literature what this value actually represents with respect to OC alone. The EC percentage averages from this study were in line with profile 22061. The presence of SO_4 and NO_3 in the results from this study averaged less than 1% of the PM2.5, which is in line with the SO_4 and NO_3 split factors in profile 22061.

Table 5.3. Residential Wood Combustion PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
Fireplace: Pine	56.0 ± 2.8	1.4 ± 0.1	0.12 ± 0.01	0.19 ± 0.01	Schauer, J.J., M.J. Kleeman, G.R. Cass, B.R.T. Simoneit. Measurement of Emissions from Air Pollution Sources. 3. C_1-C_{29} Organic Compounds from Fireplace Combustion of Wood. Environmental Science and Technology, vol. 35, pp. 1716-1728, 2001.
Fireplace: Oak	59.1 ± 3.0	3.2 ± 0.2	0.41 ± 0.01	0.44 ± 0.01	Same
Fireplace: Eucalyptus	43.7 ± 2.2	2.6 ± 0.2	0.24 ± 0.01	0.45 ± 0.01	Same

The split factors in Table 5.3 were developed by burning each type of wood in a residential fireplace. The hot exhaust from the chimney at a level approximately 5 meters above the flame was drawn isokinetically through a cyclone separator to remove particles with an aerodynamic diameter >10μm. Particles <10μm then passed through a heated stainless steel tube and through a venturi meter. Next, the emission stream was mixed with HEPA and activated carbon filtered dilution air to bring the mixture to ambient temperature and pressure. Most of the emission stream was then passed through a quartz fiber filter. The remaining portion of the

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emission stream was sent to a residence time chamber where the semivolatile compounds were allowed time to reach equilibrium between gas and particle phases. After sufficient time in the residence chamber, the emission stream was drawn through four AIHL cyclone separators to remove particles >1.8μm. Gases and fine particles <1.8μm passed through the cyclones and were then directed to a series of sampling trains operated in parallel.

Analysis of the samples collected from this study yielded split factors for OC, SO_4, and NO_3 that were not significantly different than split factor profile number 22061. The EC split factor from this study is roughly 2.4%, which is much lower than the 10.77% EC split factor in split factor profile 22061.

Table 5.4. Residential Wood Combustion PM2.5 Emission Rates and Estimated PM2.5 Split Factors

Profile Name	OC 1. mg/kg wood burned 2. estimated split factor percent	EC 1. mg/kg wood burned 2. estimated split factor percent	SO4 1. mg/kg wood burned 2. estimated split factor percent	NO3 1. mg/kg wood burned 2. estimated split factor percent	Reference Information
Fireplace: Softwood *(TOR Method)*	1. 3007.28 ± 333.54 2. 59%	1. 774.15 ± 69.67 2. 15%	1. 10.20 ± 3.33 2. 0.2%	1. 6.80 ± 1.42 2. 0.1%	McDonald, J.D., B. Zielinska, E.M., Fujita, J.S. Sagebiel, J.C. Chow, J.G. Watson. Fine Particle and Gaseous Emission Rates from Residential Wood Combustion. Environmental Science and Technology, vol. 34, pp. 2080-2091, 2000.
Fireplace: Hardwood *(TOR Method)*	1. 3579.95 ± 798.12 2. 63%	1. 397.52 ± 117.67 2. 7%	1. 27.51 ± 15.11 2. 0.5%	1. 9.94 ± 3.41 2. 0.2%	Same
Woodstove: Hardwood *(TOR Method)*	1. 2821.09 ± 1770.64 2. 60%	1. 356.33 ± 216.86 2. 8%	1. 26.64 ± 14.62 2. 0.6%	1. 0.59 ± 3.83 2. 0.01%	Same
Fireplace: Synthetic Log *(TOR Method)*	1. 1087.61 ± 108.75 2. 13%	1. 6578.23 ± 474.97 2. 79%	1. 0.00 ± 2.98 2. 0%	1. 2.24 ± 3.00 2. 0.03%	Same

The split factors in Table 5.4 were developed by burning each type of wood in a residential woodstove or fireplace (as noted next to each split factor profile). Duplicate runs of each of the four split factor profile types were run to vary conditions such as the use of a grate in the fireplace, burn rate, and fuel moisture content. The fireplace used in this study was a Heatilator model E36 fireplace with or without a model GR4 grate. The woodstove used in this study was a noncatalytic Pineridge woodstove. The samples were collected by a dilution stack sampler equipped with a 2.5μm particle selective cyclone. The emissions were diluted 20-70 times and brought to ambient temperature. A residence time of 80 seconds was allowed so that condensation could occur prior to collection of the particles. Fine particulate and semivolatiles were collected on filter/PUF/XAD/PUF cartridges, and inorganics were collected on Teflon and quartz filters. The particulate and semivolatile analysis was conducted by gas chromatography/mass spectrometry (GC/MS). The Teflon filter mass was measured by

gravimetry. Quartz filters were analyzed for EC and OC using thermal/optical reflectance (TOR), and ions were measured by ion chromatography (IC).

The emission rates (mg PM2.5/kg wood burned) for each of the tests in this study were included in tables in the literature. It was necessary for PES to calculate the estimated split factor for each of the four species (EC, OC, SO_4, and NO_3) by dividing the emission rate of each species by the total PM2.5 emission rate. The total PM2.5 emission rate for each of the four combustion scenarios included in this study was 5.1g/kg for softwoods burned in the fireplace, 5.7g/kg for hardwoods burned in the fireplace, 4.7g/kg for woodstove emissions, and 8.3g/kg for burning of the synthetic log. Since the uncertainty of the total PM2.5 emission rate was not quantified in the literature, it was not possible to calculate the uncertainty of the split factor calculations.

A comparison of the results from this study with split factor profile 22061 shows that synthetic log burning yields different results than the burning of natural wood in a woodstove or fireplace. The EC and OC split factors from the synthetic log test were completely different than the results from the other tests conducted. The emissions from the woodstove and fireplace in this study were somewhat different from each other but not enough data were available in the article to determine how much of the difference was due to the varied conditions that were applied to both the fireplace and woodstove tests. Disregarding the synthetic log test, the fireplace and woodstove OC split factors from this article average roughly 61% compared to the split factor profile 22061 OC split factor of 47.13%. The EC split factors from this article average roughly 10% which is in agreement with the EC split factor of 10.77% in split factor profile 22061.

Two other articles contained some information on PM2.5 emissions from residential wood combustion, but the EC, OC, SO_4 and NO_3 split factors were not explicitly provided and there was not sufficient information to calculate them. The two articles are as listed below:

Reference 1. Kleeman, M.J., J.J. Schauer, G.R. Cass. Size and Composition Distribution of Fine Particulate Matter Emitted from Wood Burning, Meat Charbroiling, and Cigarettes. Environmental Science and Technology, vol. 33, pp. 3516-3523.

Reference 2. Purvis, C.R., R.C. McCrillis. Fine Particulate Matter (PM) and Organic Speciation of Fireplace Emissions. Environmental Science and Technology, vol. 34, pp. 1653-1658.

Recommendations for Revisions to the Residential Wood Combustion Profile

There are no suggested revisions to the current residential wood combustion profile at this time due to the variability of the profiles included in this report. There are several methods used to collect data for the studies included in this report and since each study is somewhat different the results are not comparable.

Non-road Diesel

Split factors pertaining to PM2.5 emissions from non-road diesel engines were not located in the literature search.

Solid Waste Combustion

Split factors pertaining to PM2.5 emissions from solid waste combustion were not located in the literature search.

Coal Combustion

PES researched recent literature to locate split factor emission profiles for coal combustion. Two of the articles that were located contained split factor profile data. These data are summarized in Table 6. Other articles that were reviewed contained information on PM2.5 from coal combustion, but did not contain split factors or the data necessary to determine split factors. Articles that were reviewed but did not contain split factor data are listed below.

Reference 1. Shoji, T., F. E. Huggins, G.P. Huffman. XAFS Spectroscopy Analysis of Selected Elements in Fine Particulate Matter Derived from Coal Combustion. Energy and Fuels, vol. 16, pp. 325-329, 2002.

Reference 2. Linak, W.P, C.A. Miller, J.O.L. Wendt. Comparison of Particle Size Distributions and Elemental Partitioning from the Combustion of Pulverized Coal and Residual Fuel Oil. Journal of the Air and Waste Management Association, vol. 50, pp. 1532-1544, 2000.

Table 6. Coal Combustion PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
Coal-Fired Boiler 550 MW with baghouse and wet limestone scrubber Profile ID: CFPP1 *(TOR Method)*	62.8505 ± 14.8165	2.7238 ± 3.2386	11.4070 ± 2.0918	2.5397 ± 1.0346	Chow, J.C. et. al.; Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Coal-Fired Boiler 600 MW with baghouse and wet limestone scrubber Profile ID: CFPP2 *(TOR Method)*	55.6750 ± 11.9389	2.3686 ± 4.0871	5.7416 ± 1.9133	0.9998 ± 0.6741	Chow, J.C. et. al.; Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Coal-Fired Boiler 600 MW with baghouse and wet limestone scrubber Profile ID: CFPP3 *(TOR Method)*	22.8083 ± 4.1552	0.6386 ± 0.9373	9.4809 ± 2.7967	0.0735 ± 0.1819	Chow, J.C. et. al.; Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.

Table 6. Coal Combustion PM2.5 Split Factors (continued)

Profile Name	OC Percent	EC Percent	SO₄ Percent	NO₃ Percent	Reference Information
Coal-Fired Boiler 545 MW at Al process facility with dry limestone scrubber Profile ID: CFPP4 *(TOR Method)*	4.1699 ± 1.5348	1.5787 ± 0.7776	45.6284 ± 18.6921	0.0676 ± 0.0514	Chow, J.C. et. al.; Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Coal-Fired Boiler 550 MW with ESP and baghouse Profile ID: CFPP5 *(TOR Method)*	10.3044 ± 9.7720	0.1321 ± 0.7674	46.2367 ± 6.8494	0.0904 ± 0.0844	Chow, J.C. et. al.; Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Coal-Fired Boiler Profile ID: CFPP Composite *(TOR Method)*	27.1762 ± 25.7663	1.3836 ± 2.2247	28.7433 ± 22.5634	0.6865 ± 1.0917	Chow, J.C. et. al.; Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.
Eastern U.S. Coal *(TOR Method)*	2.94 ± 0.53	0.31 ± 0.08	3.07 ± 0.15	NR	Lee, W.S.; Source Profiles of Particulate Matter Emissions From a Pilot-Scale Boiler Burning North American Coal Blends. Air and Waste Management Association, vol. 51, pp. 1568-1578, 2001.
Highvale Coal *(TOR Method)*	8.36 ± 0.48	0.44 ± 0.03	4.35 ± 0.21	NR	Lee, W.S.; Source Profiles of Particulate Matter Emissions From a Pilot-Scale Boiler Burning North American Coal Blends. Air and Waste Management Association, vol. 51, pp. 1568-1578, 2001.
Coal Valley Coal *(TOR Method)*	7.33 ± 0.45	0.18 ± 0.02	4.44 ± 0.22	NR	Lee, W.S.; Source Profiles of Particulate Matter Emissions From a Pilot-Scale Boiler Burning North American Coal Blends. Air and Waste Management Association, vol. 51, pp. 1568-1578, 2001.

 "NR" = "Not Reported"

The five unique profiles and one composite profile from the BRAVO study (Chow, et. al., 2002) were obtained from three electrical generation stations that supplied power for domestic use and from one station that supplied power to an aluminum processing facility. The boiler represented by profile CFPP4 combusted potliner material in addition to coal. Dilution stack sampling was used to collect emissions from the boilers. Emissions were sampled from the stack isokinetically through a button hook nozzle, then through a heated copper line to a u-tube where the exhaust was mixed with HEPA and activated carbon filtered dilution air at ambient temperature under turbulent flow conditions. Dilution ratios were varied from 9 to 60 times, with a typical dilution ratio of 30. The diluted air was allowed a residence time of approximately 80 seconds to condense. The diluted air was then drawn through three cyclones to a multi-port sampling manifold. The profiles were normalized to the sum of the species. OC and EC

fractions were determined by the IMPROVE thermal optical reflectance method (TOR). The individual profiles were then composited to form the six profiles addressed in the BRAVO study and this memorandum.

The profiles from the BRAVO study were compared to each other, and EPA PM2.5 split factor profile number 22001 shown in Table 2 of this report. Among the profiles from the BRAVO study, the OC split factor varied from 4-63%, the EC split factor varied from 0.13-2.72%, the SO_4 split factor varied from 6-46%, and the NO_3 split factor varied from 0.07-2.5%. The magnitude of variation between the individual BRAVO profiles is averaged in the composite profile. Comparison of the BRAVO composite profile with split factor profile 22001 shows a large difference in the OC and SO_4 split factors. The BRAVO composite OC split factor is more than one order of magnitude larger than the profile 22001 OC split factor, but also has an uncertainty almost as large as the split factor. The BRAVO composite SO_4 split factor is more than twice that of the profile 22001, and also has an uncertainty almost as large as the split factor.

The three split factor profiles from Lee, 2001 were developed from emission samples collected from combustion of three different North American coal blends using a 0.7 MW pulverized coal-fired, pilot scale boiler equipped with an electrostatic precipitator (ESP). The ESP was operated at roughly 10% less than its maximum capacity. The samples were withdrawn from the stack isokinetically, and then diluted 20 to 42 fold with clean air inside a Teflon coated tunnel. Thermal optical reflectance (TOR) was used to determine the EC and OC content, and ion chromatography (IC) was used to determine SO_4 and NO_3.

The profiles from Lee, 2001, were compared to each other and EPA PM2.5 split factor profile number 22001. The three profiles from Lee, 2001 were relatively consistent even considering the variation in coal type. The OC split factor from Lee, 2001 averaged roughly 6%, which is approximately seven times higher than the OC split factor from profile 22001. The EC split factor from Lee, 2001 averaged roughly half of the 1.83% EC split factor from profile 22001. The SO_4 split factor from Lee, 2001 was roughly 4% compared to 11.90% in split factor profile 22001, and NO_3 was not reported, which was consistent with the existing split factor.

<u>Recommendations for Revisions to the Coal Combustion Profile</u>

The split factor data included in this report represents coal combustion emissions resulting from several control scenarios, boiler sizes and configurations, making it difficult to compare to the current profile, number 22001 (See Table 2 of this report). It is apparent from examination of the profiles in Table 6, that control scenarios play a large role in determining the characteristics of the PM2.5 emissions from coal combustion. Additionally, the coal itself may be a bigger factor than the control scenario. SO_4 is probably directly related to the sulfur content of coal and whether or not there is a control device. Since only one coal combustion split factor can be used to split an entire inventory, it is necessary to derive one split factor profile from the data collected.

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Research of the background information that was used to develop the current profile for coal combustion, number 22001, showed that the profile was calculated incorrectly by switching the EC and OC amounts. Due to this switch in profile 22001, the EC split factor is represented as higher than the OC split factor in profile 22001. All the profiles shown in Table 6 of this report show that the OC split factor is higher than the EC split factor.

PES recommends using a coal combustion split factor derived from the average of the BRAVO composite profile averaged with a composite of the profiles from Lee, 2001. The profile resulting from this method of calculation would have the following values: OC: 17%, EC: 1%, SO_4: 16%, and NO_3: 0.5%.

On-road HDDV

PES researched recent literature to locate split factor emission profiles for on-road heavy duty diesel vehicles (HDDV). Several articles were located, but many of them did not contain usable speciated PM2.5 data, or were considered inapplicable. Other articles that were found did not specifically address HDDVs. In an effort to include all information that could be used to improve the quality of split factors for HDDVs, PES followed up with James Schauer, one of the authors of an article on medium duty diesel vehicles (MDDV) to determine whether that data could be considered comparable to emission data from HDDVs. Mr. Schauer replied that an effort to determine the best split factor profile for diesel exhaust is currently under way, and the results will be available by Fall 2003. The current effort involves the "average driving cycle" approach which studies the emissions from vehicles at various loads and engine speeds. PM particle size distribution and chemical composition vary greatly depending on the load and engine speed, so it is a challenge to develop one profile that represents the average driving cycle of HDDVs. PES has included the split factors from MDDV in this memorandum for comparison to the EPA's existing split factor profile number 35600, and other HDDV split factors.

Two articles that were located, but did not contain usable speciated PM2.5 data are listed below.

Reference 1: Westerholm, R.N., J. Almen, H. Li, J.U. Rannug, K. Egeback, K. Gragg. Chemical and Biological Characterization of Particulate-, Semivolatile-, and Gas-Phase-Associated Compounds in Diluted Heavy-Duty Diesel Exhausts: A Comparison of Three Different Semivolatile-Phase Samplers. Environmental Science and Technology, vol. 25, pp. 332-338, 1991.

Reference 2: Kweon, C., D.E. Foster, J.J. Schauer, S. Okada. Detailed Chemical Composition and Particle Size Assessment of Diesel Engine Exhaust. Society of Automotive Engineers, Inc., 2002.

Another article that was located, but not included in this memorandum is listed below. The reason the article is discounted is because the information is based on an engine study conducted in the United Kingdom, using diesel fuel with a composition different than what is used in the United States.

Shi, J.P., D. Mark, R.M. Harrison. Characterization of Particles from a Current Technology Heavy-Duty Diesel Engine. Environmental Science and Technology, vol. 34, pp. 748-755, 2000.

Table 7. HDDV PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
HDDV Diesel Bus – No Particulate Trap *(TOR Method)*	29.6 ± 3.0	53.4 ± 6.4	9.2 ± 1.4	0.09 ± 0.01	Lowenthal, D.H., B. Zielinska, J.C. Chow, J.G. Watson, M. Gautam, D.H. Ferguson, G.R. Neuroth, K.D. Stevens. Characterization of Heavy-Duty Diesel Vehicle Emissions. Atmospheric Environment, vol. 28, no. 4, pp. 731-743, 1994.
HDDV Diesel Bus – Particulate Trap *(TOR Method)*	66.7 ± 6.0	5.2 ± 3.5	13.4 ± 5.4	0.08 ± 0.07	Lowenthal, D.H., B. Zielinska, J.C. Chow, J.G. Watson, M. Gautam, D.H. Ferguson, G.R. Neuroth, K.D. Stevens. Characterization of Heavy-Duty Diesel Vehicle Emissions. Atmospheric Environment, vol. 28, no. 4, pp. 731-743, 1994.
HDDV Jet A Fuel Bus – No Particulate Trap *(TOR Method)*	44.8 ± 16.2	49.9 ± 17.8	2.4 ± 1.2	0.21 ± 0.24	Lowenthal, D.H., B. Zielinska, J.C. Chow, J.G. Watson, M. Gautam, D.H. Ferguson, G.R. Neuroth, K.D. Stevens. Characterization of Heavy-Duty Diesel Vehicle Emissions. Atmospheric Environment, vol. 28, no. 4, pp. 731-743, 1994.
HDDV Jet A Fuel Bus – Particulate Trap *(TOR Method)*	68.6 ± 22.3	22.2 ± 22.1	4.8 ± 4.6	1.06 ± 1.10	Lowenthal, D.H., B. Zielinska, J.C. Chow, J.G. Watson, M. Gautam, D.H. Ferguson, G.R. Neuroth, K.D. Stevens. Characterization of Heavy-Duty Diesel Vehicle Emissions. Atmospheric Environment, vol. 28, no. 4, pp. 731-743, 1994.
HDDV Diesel Truck – No Particulate Trap *(TOR Method)*	35.4 ± 17.8	43.3 ± 20.1	14.2 ± 8.0	0.06 ± 0.04	Lowenthal, D.H., B. Zielinska, J.C. Chow, J.G. Watson, M. Gautam, D.H. Ferguson, G.R. Neuroth, K.D. Stevens. Characterization of Heavy-Duty Diesel Vehicle Emissions. Atmospheric Environment, vol. 28, no. 4, pp. 731-743, 1994.
HDDV Jet A Truck – No Particulate Trap *(TOR Method)*	26.8 ± 16.5	61.1 ± 13.7	4.0 ± 3.5	0.35 ± 0.20	Lowenthal, D.H., B. Zielinska, J.C. Chow, J.G. Watson, M. Gautam, D.H. Ferguson, G.R. Neuroth, K.D. Stevens. Characterization of Heavy-Duty Diesel Vehicle Emissions. Atmospheric Environment, vol. 28, no. 4, pp. 731-743, 1994.
MDDV Diesel Truck	19.7 ± 1.6	30.8 ± 2.6	1.00 ± 0.25	0.01 ± 0.01	Schauer, J.J., M.J. Kleeman, G.R. Cass, B.R.T. Simoneit. Measurement of Emissions from Air Pollution Sources 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks. Environmental Science and Technology, vol. 33 pp 1578-1587, 1999.

In the study by Lowenthal et. al., 1994, the emissions from 13 HDDV trucks and busses were measured at the Phoenix Transit Yard in Phoenix, AZ in 1992. The West Virginia University Transportable HDDV Testing Laboratory (Mobile Lab) was used to conduct the tests of the individual vehicles. Two different types of fuel were used, and some of the vehicles were

equipped with particulate traps (noted in Table 7). The Mobile Lab tested the vehicles over the Central Business District (CBD) driving cycle while the exhaust was sampled from a total exhaust dilution tunnel. Aerosols were collected over a 30 minute period (three 10-minute tests) on a Teflon membrane filter at temperatures of 80-90° F. The filters were weighed to determine aerosol mass, and then analyzed using x-ray fluorescence (XRF). Additionally, one-half of the filter was analyzed for SO_4 and NO_3 using ion chromatography (IC), and OC and EC were analyzed using thermal/optical reflectance (TOR). The split factors from the study were reported as a mean ± standard deviation.

A comparison of the results from Lowenthal et. al., 1994, to split factor profile 35600 shows that although there are a wide range of results in Lowenthal, et. al., 1994, the trend is much different than that of split factor profile 35600. The OC split factor reported by Lowenthal, et. al., 1994, is consistently higher than the 18.91% OC split factor in split factor profile 35600. Likewise, the EC split factor reported by Lowenthal, et. al., 1994, is lower than the 75.00% EC split factor in split factor profile 35600. The SO_4 split factor reported by Lowenthal, et. al., 1994, is consistently higher than the 0.41% SO_4 split factor in split factor profile 35600. This could be due to a different fuel chemical consistency used in this 1992 test compared with the fuel used in the test to develop split factor profile 35600, which was based on a 1996 study. The NO_3 split factor reported by Lowenthal et. al., 1994, is not significantly different than split factor profile 35600.

The results from Schauer et. al., 1999, are based on a study conducted to quantify and speciate the fine particulate emissions from medium duty diesel vehicles (MDDV). A two-stage dilution source sampling system was used to collect tailpipe emissions from vehicles driven through the hot-start Federal Test Procedure (FTP) urban driving cycle on a transient chassis dynamometer. The emissions from the trucks were diluted with HEPA and activated carbon filtered air. Particles larger than 10μm were then removed by a cyclonic separator. Next, the gas-phase and particulate matter that passed through the cyclonic separator were passed through a venturi meter and into the primary sampling system where they were diluted for a second time. The two dilution stages combined result in a total dilution of approximately 140 fold. In the first sampling train, the emissions pass through another cyclonic separator followed by a XAD-coated denuder, then through three quartz fiber filters operated in parallel and finally through two polyurethane foam (PUF) cartridges. Four copies of a second sampling train are used for collection of semivolatile organics and particulate material. Additionally, a third type of cyclone based sampling unit is operated consisting of two quartz filters used to analyze EC and OC content by thermal evolution and combustion analysis. Inorganic ions are collected on a Teflon membrane filter and measured using ion chromatography (IC).

The split factors developed by Schauer et. al., 1999, are similar in comparison to split factor profile 35600. The EC split factor was the only factor that was significantly different from profile 35600. Schauer et. al., 1999, reported an EC split factor of 30.8 ± 2.6, compared to the EC split factor of 75.00% in profile 35600.

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Recommendations for Revisions to the On-road HDDV Profile

Comparison of split factor profile 35600 in Table 2, to the split factor profiles in Table 7 shows that the results from diesel vehicles vary widely depending on the vehicle size, fuel type, and control scenarios. No background information on profile 35600 was available to determine the studies that were used to compile profile 35600. The overall trend of the profiles presented in Table 7 shows that 35600 may be underestimating the contribution of the OC split factor and overestimating the contribution of the EC split factor. The NO_3 split factor from On-road HDDV is consistent between profile 35600 and the profiles presented in Table 7. The SO_4 split factor is largely dependent on the fuel sulfur content.

Rather than revising the On-road HDDV profile at this time, PES suggests following up with the current "average driving cycle" study being conducted by James Shauer. The results of this study will be based on combustion of current diesel fuels during typical driving cycle activities.

Sand and Gravel

Split factors pertaining to PM2.5 emissions from sand and gravel were not located in the literature search.

Paved Road Dust

PES researched recent literature to locate split factor emission profiles for paved roads. Four profiles were located in two technical papers. These profiles are shown in Table 8, and discussed below.

Table 8. Paved Road PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
Paved Road Dust Craig, CO Profile ID: MZCPVRDC *(TOR Method)*	7.73 ± 2.21	1.12 ± 0.30935	0.07922 ± 0.05478	0.00000 ± 0.05451	Watson, J.G., J.C. Chow, J.E. Houck; PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere vol. 43, pp. 1141-1151. 2001.
Paved Road Dust Steamboat Springs, CO Profile ID: MZSPVRDC *(TOR Method)*	7.05 ± 3.44	0.43691 ± 0.31744	0.04942 ± 0.03804	0.03151 ± 0.05458	Watson, J.G., J.C. Chow, J.E. Houck; PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere vol. 43, pp. 1141-1151. 2001.
Composite of Paved Road Dust from Craig and Steamboat Springs, CO Profile ID: MZPVRDC *(TOR Method)*	7.39 ± 2.61	0.77971 ± 0.43154	0.06432 ± 0.04716	0.01576 ± 0.04717	Watson, J.G., J.C. Chow, J.E. Houck; PM2.5 Chemical Source Profiles for Vehicle Exhaust, Vegetative Burning, Geological Material, and Coal Burning in Northwestern Colorado During 1995. Chemosphere vol. 43, pp. 1141-1151. 2001.
Paved Road Dust – San Antonio and Laredo, TX Profile ID: BVPVRD1 *(TOR Method)*	15.8664 ± 3.1864	2.3505 ± 1.7110	0.9993 ± 0.2203	0.1104 ± 0.2066	Chow, J.C. et. al.; Source Profiles from the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. Report Prepared for Environmental Science and Technology, 2002.

The PM2.5 test samples from Watson, Chow, and Houck, 2001 were collected in the vicinity of the Yampa Valley in northwestern Colorado in 1995. The samples were collected in one-half to 1.0 kg amounts from the locations described in Table 8. The dust was stored in polyethylene bags, and prepared for testing by drying and then passing the dust through a sieve. The samples were tested by resuspending them in a laboratory chamber and sampling through PM2.5 inlets onto Teflon-membrane and quartz fiber filters. The filters were analyzed for mass by gravimetry. Next, half of each quartz fiber filter was extracted in deionized distilled water and analyzed for NO$_3$ and SO$_4$ using ion chromatography. The other half of the filter was used to quantify OC and EC using the IMPROVE thermal optical reflectance method (TOR). Potassium carbonate backup filters were extracted in a sodium carbonate solution and analyzed for absorbed SO$_2$ as SO$_4$ by ion chromatography. Silver nitrate impregnated cellulose fiber filters were analyzed for H$_2$S as SO$_4$ by ion chromatography. All sampling procedures followed an established laboratory sample chain of custody and data validation process. Blank and replicate analyses were performed for approximately 10% of all samples according to standard operating procedures.

The split factor profiles from Watson, et. al., 1995 were compared to EPA split factor profile 22058. The three Watson, et. al. profiles show consistent split factor results that only differ significantly with respect to the OC split factor. The OC split factor from split factor profile 22058 is reported as 14.73%, but all three of the Watson, et. al., 1995 profiles report an OC split factor of roughly 7%.

The PM2.5 test samples from the BRAVO study (Chow et. al. 2002) were collected at various intersections in San Antonio and Laredo, TX in 1999. The samples were obtained by the grab/resuspension method, air dried in the laboratory under 20-30% relative humidity atmosphere, sieved through a Tyler 400 mesh screen ($< 38\mu m$ geometric diameter), and resuspended in a laboratory chamber. The PM was collected on filters through PM2.5 and PM10 impactor inlets at a flow rate of 10 L/min. Chemical abundances for each sample were determined by dividing the concentration of each chemical by the total mass concentration, with error propagation calculated by addition in quadrature. The individual profiles were then composited to form the paved road dust profile addressed in the BRAVO study and this memorandum. OC and EC fractions were determined by the IMPROVE thermal optical reflectance method (TOR).

The paved road dust profile from the BRAVO study compares well to split factor profile 22058. The values for all four split factors are the same as split factor 22058 within the uncertainty of the estimates.

Recommendations for Revisions to the Paved Road Dust Profile

Comparison of the profiles presented in Table 8 with the current split factor profile, number 22058 points to a need for revision of the current profile. As discussed in a previous report titled: "Expansion of Existing PM2.5 Split Factor Background Documentation", there were some mistakes in the calculation of the NO_3 split factor for profile 22058. The NO_3 factor is probably even closer to zero than 0.22% as reported by profile 22058. PES suggests revising the NO_3 factor to the average of the profiles in Table 8: 0.04%. Additionally, since the OC and EC from profile 22058 were based on only one split factor profile, PES recommends revising the current split factors for OC and EC to the averages from the profiles reported in Table 8. This will result in the OC and being changed to 10%, and no change to the EC factor.

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Wood Waste Boiler

No wood waste boiler profiles were found in the results from a recent literature search; however, a recent EPA publication on wood-fired industrial boilers was supplied by the EPA. The results from this publication are included in Table 9.

Table 9. Wood Waste Boiler PM2.5 Split Factors

Profile Name	OC Percent	EC Percent	SO$_4$ Percent	NO$_3$ Percent	Reference Information
Industrial Wood-Fired Boiler with denuder *(TOE Method)*	32.6 ± 8.0	13.8 ± 3.1	7.8 ± 0.6	NQ	EPA-600/R-01-106; Source Sampling Fine Particulate Matter: Wood-Fired Boiler. Report prepared for The Office of Air Quality Planning and Standards, December, 2001.
Industrial Wood-Fired Boiler without denuder *(TOE Method)*	84.6 ± 11.0	3.0 ± 0.4	7.8 ± 0.6	NQ	EPA-600/R-01-106; Source Sampling Fine Particulate Matter: Wood-Fired Boiler. Report prepared for The Office of Air Quality Planning and Standards, December, 2001.

"NQ" = Below quantifiable limits

The study used to develop the profiles in Table 9 was conducted in August 2000 using an industrial wood-fired boiler equipped with an ESP control device. Dilution source sampling was used to collect the emissions from the boiler. As the emissions were drawn into the sample inlet zone, they first passed through a cyclonic separator which removed the particles >10μm. Next the emissions were passed through a venturi meter, and then mixed in a turbulent mixing chamber. The emissions continued into a residence chamber for approximately 60 seconds. After that time the samples were collected from the sample ports. Teflon filters were used to collect PM samples for mass determination and inorganic ion analysis. The inorganic ion analysis including SO$_4$ and NO$_3$ was conducted using ion chromatography (IC). Quartz filters were used to collect samples for EC and OC analysis which was conducted using thermal/optical evolution (TOE). As shown in table 9, one profile represents the results from the use of a denuder to remove organic gases prior to the quartz EC/OC filter, the other profile represents the same sampling technique, but without the denuder.

The split factors from the two wood-fired boiler profiles were compared to split factor profile 22008. Both of the wood-fired boiler profiles were significantly different than split factor profile 22008 with respect to OC, EC, and SO$_4$. NO$_3$ was not quantified in the EPA report, but is only reported as 0.09% in split factor profile 22008, so the difference between the profiles is relatively insignificant. In general, the profiles from the recent EPA report contain OC split factors several times greater than the 9.81% reported in split factor profile 22008. The EC from the EPA report was lower than split factor profile 22008 in both cases. The SO$_4$ split factor from the recent EPA report was more than twice the SO$_4$ split factor from split factor profile 22008.

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Recommendations for Revisions to the Wood Waste Boiler Profile

As discussed above, the profiles from the EPA document show a significant difference in split factor characteristics compared to the current split factor profile, number 22008. The information used to develop profile 22008 is from two reports published in 1979 and 1983. Since only two reports were used to develop profile 22008 and the information is dated, PES recommends use of the new information published in the 2001 EPA report, and included in Table 9. The profile from the sample taken with the denuder should be used since this profile represents the PM2.5 sample without the inclusion of additional organic gases. The suggested profile has the following values: OC: 33%, EC: 14%, SO_4: 8%, and NO_3: 0%.

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